CO_2 Sequestration via Mineralization: *In Situ* Reaction Studies in "Above Ground" and Geological setting

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Background:

- Mineral Sequestration Working Group (NETL-DOE) (1998-2005)
- **ASU:** 4 faculty, 2 postdocs, 3 grad students, 2 undergrads
- **Specialization:**

  - atomic level mechanistic process analysis
  - *in situ* process characterization
  - atomic level property/reaction simulations
  - multi-phase fluid dynamics simulations

- **Current Support:**

  DOE-NETL, Argonne National Laboratory, ORICA

Areas of particular interest include:

- Fluid/solid reaction mechanisms

- Optimization of mineral carbonation reactions

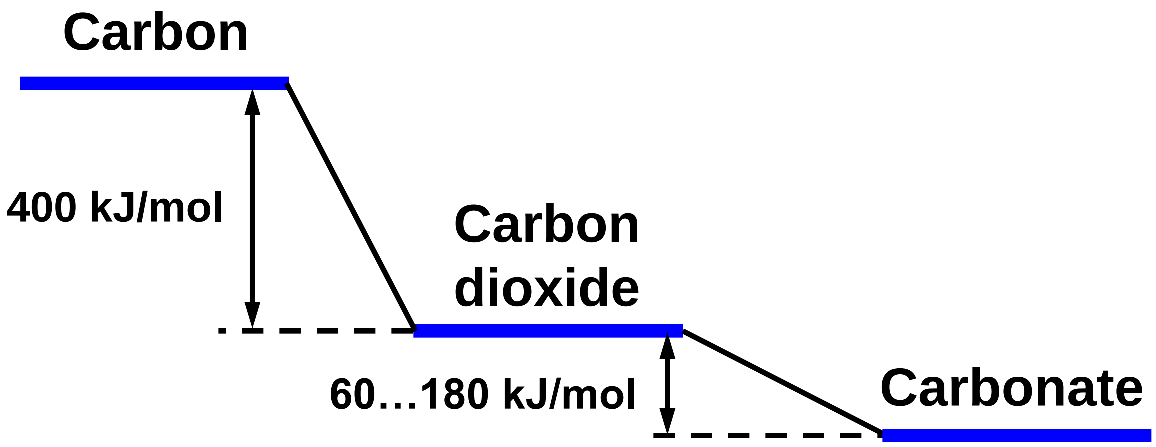
- Pressure and temperature dependence of key solution species' activities and the formation mechanism (including kinetics) of solid carbonate phases and their aqueous complexes

- Diffusion rates of carbon-bearing species in solution and porous minerals

- Ex-situ vs in-situ comparisons of aqueous CO_2-mineral interactions in geological sequestration setting

Mineral Sequestration of CO_2:

The ground state energy of **carbon** is a **mineral carbonate**



http://www.fossil.energy.gov/news/techlines/2001/tl_arc_sequestration.html

"Magnesite" - $MgCO_3$

Mineral Sequestration of CO_2:

Permanent

Kaibab limestone layer ($CaCO_3$)

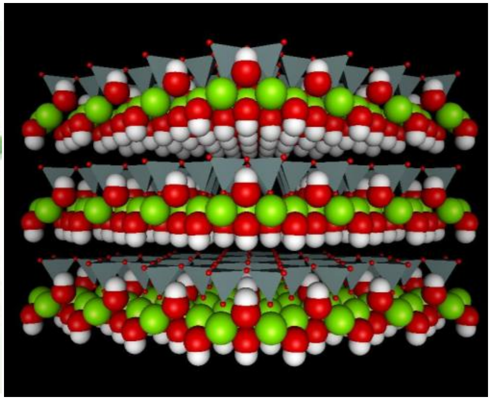
"Mineral Sequestration" carbonate product:

- environmentally benign
- stable on geological time scale
- no monitoring costs
- mimics natural weathering processes in rocks

Mineral Carbonation Reactions

General Reactions: $(Mg, Ca)_x Si_y O_{x+2y+z} H_{2z} + xCO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2 + zH_2O$

Serpentine



$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$

MgO: 38-45 wt %

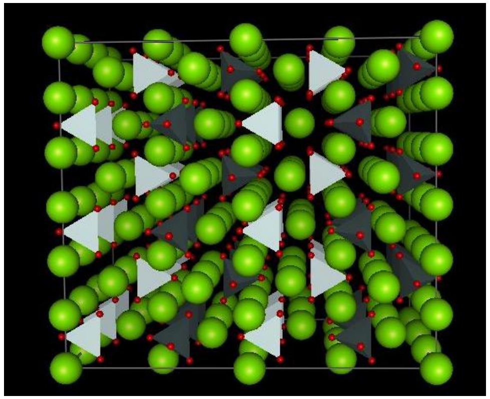
Iron oxides: 5-8 wt %

Water: 13 wt %

Exothermic reaction: **+64 kJ/mole**

One ton to dispose of 1/2 ton of CO_2

Olivine



$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$

MgO: 45-50 wt %

Iron oxides: 6-10 wt %

Exothermic reaction: **+95 kJ/mole**

One ton to dispose of 2/3 ton of CO_2

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Aqueous Mineral Carbonation Process
(DOE/NETL Albany Research Center)

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \xrightarrow[150\ ^oC\ +\ 150\ atm\ CO_2]{1M\ NaCl\ +\ 0.64\ M\ NaHCO_3} 3MgCO_3 + 2SiO_2 + 2H_2O$$

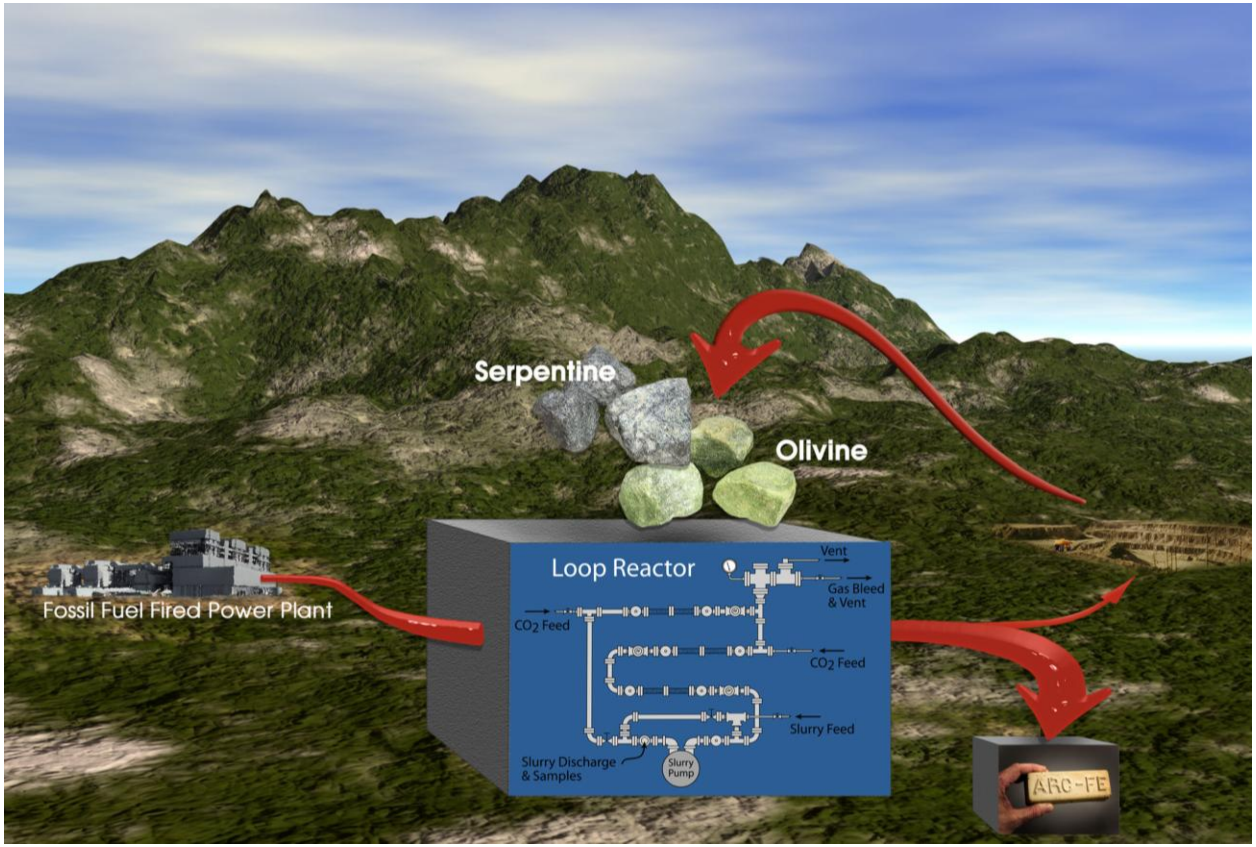
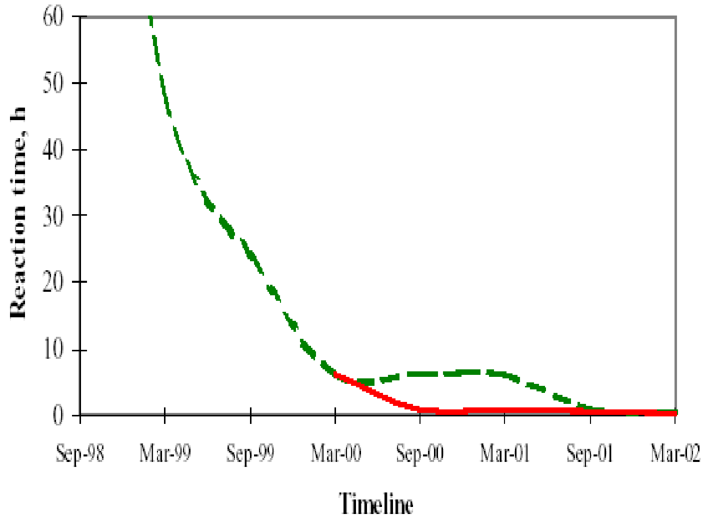


Illustration: DOE/NETL Albany Research Center

Progress…



Aqueous process (Albany Research Center):

→ 0.64 *M* $NaHCO_3$ + 1 *M* NaCl

- Sodium bicarbonate increases HCO_3^- concentration
- NaCl may help release Mg ions from silicate
- Current status: >85 % conversion achieved in 20-30 minutes @ 185 bar, & 120 ^{0}C

- Heat **pre-treatment** (600-650^{o}C) of **serpentine** removes chemically-bonded water and creates "open" structure…
- Various types of **mechanical attrition** improve reaction in **olivine** feedstock…
- Pretreament is energy intensive!

Goal is to develop the atomic level understanding needed to improve carbonation reaction rates and reduce process cost

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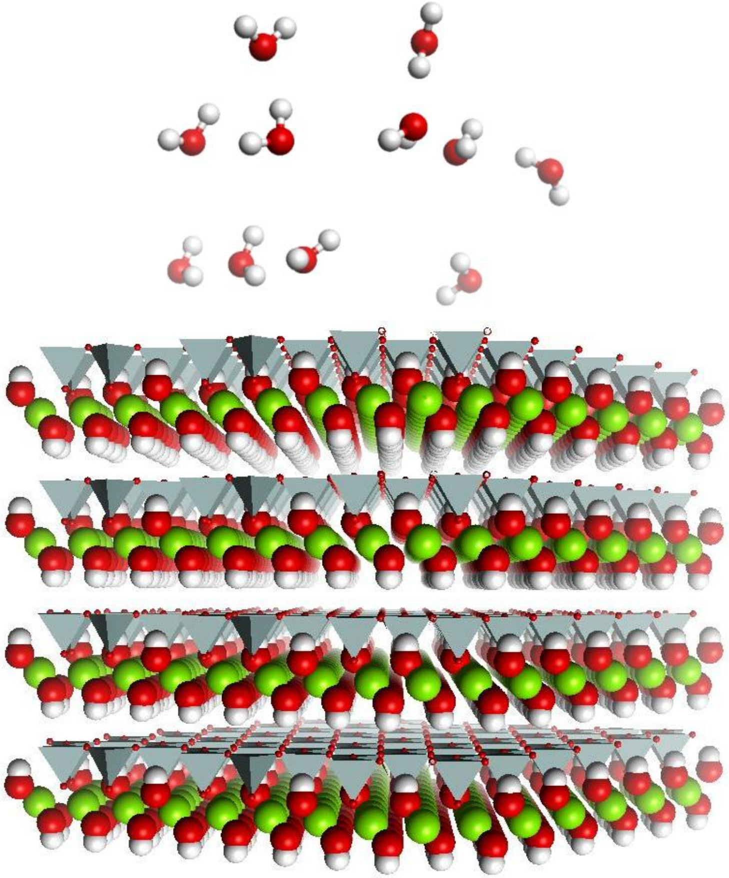
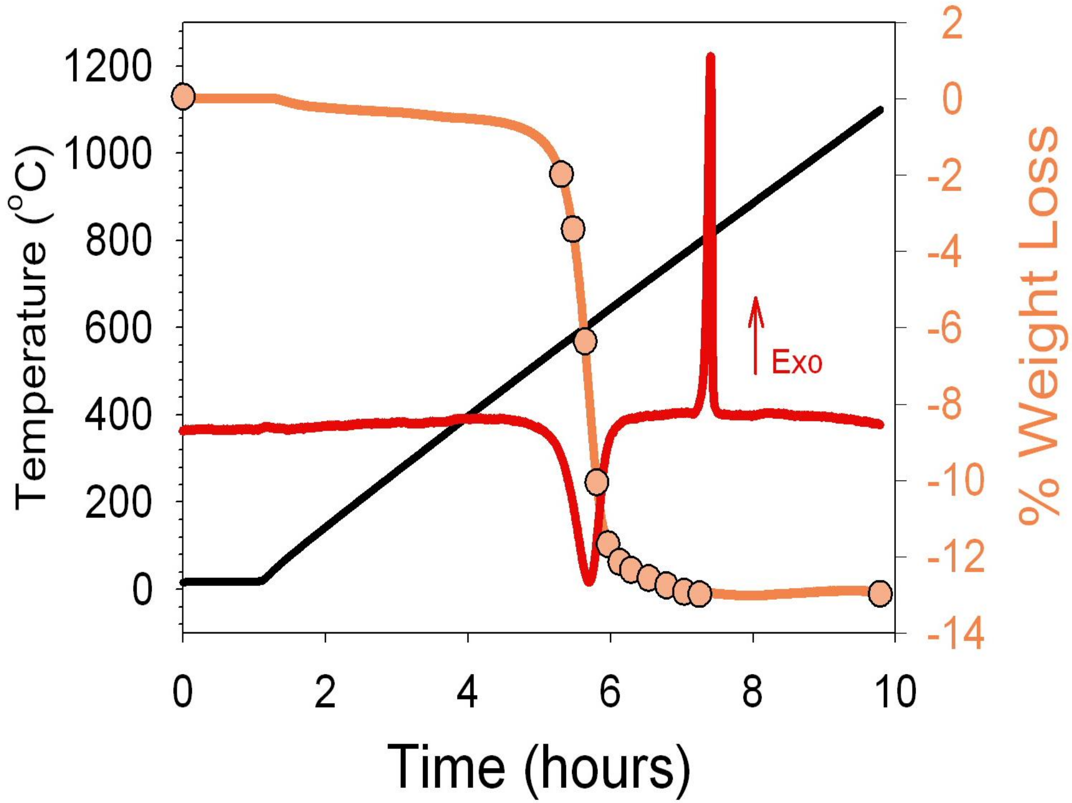
"Roasting" serpentine releases H_2O to produce a reactive meta-serpentines feedstock



$Mg_3Si_2O_5(OH)_4 \rightarrow Mg_3Si_2O_{5+2x}(OH)_{4-4x} + 2x(H_2O)$



This talk:

- Development of specialized ***microreactor*** cells which allow study of mineral (above-ground) and geological (below-ground) sequestration processes over a broad range of P and T conditions using:

  - x-ray synchrotron
  - nuclear magnetic resonance
  - Raman spectroscopy

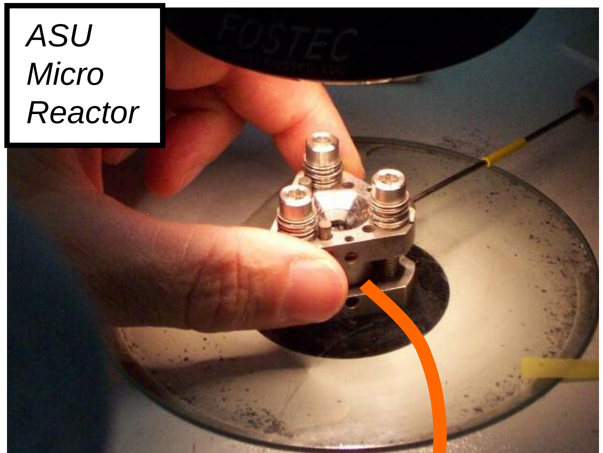
- Use first principles quantum chemical simulations (and supercomputers) to elucidate structure-property relationships and process mechanisms.

Examples:

- mineral sequestration
- hydrous carbonate phase formation
- temperature/pressure dependence of CO_2 reactions
- aqueous diffusion rates of sequestration species

RECENT ADVANCES in CARBON SEQUESTRATION at ASU:

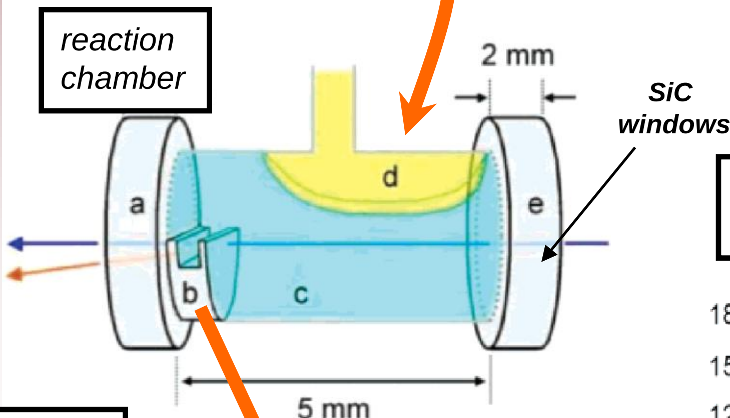
DEVELOPMENT OF A CHEMICAL MICRO-REACTOR for IN-SITU REACTION STUDIES

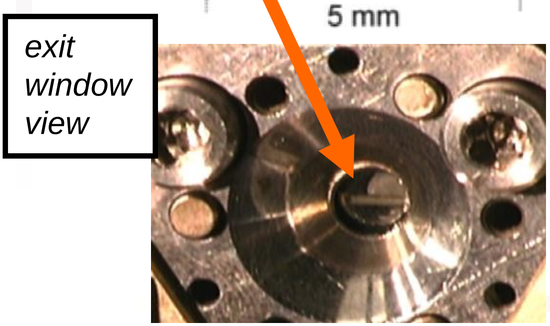


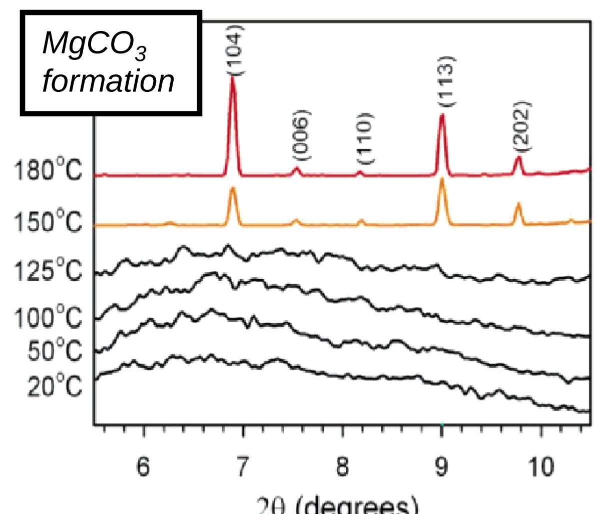
- Moissanite (single crystal SiC) window technology enables spectroscopic access to chemical processes up to T=400 ^{o}C and P=350 atm.

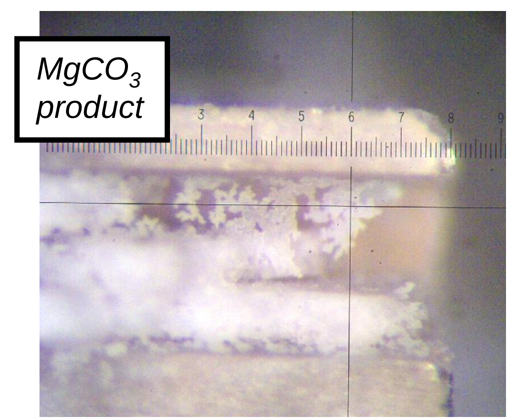
- Use large external ballast to maintain **constant chemical activity** as reactants are consumed (e.g., unlike closed autoclave systems).

- *in situ* monitoring of reactions allows parameter space to be quickly and accurately mapped (see $MgCO_3$ formation below).









ASU experiments performed at the GeoSoilEnviroCARS synchrotron beamline (Argonne National Laboratory)

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Argonne National Laboratory Synchrotron

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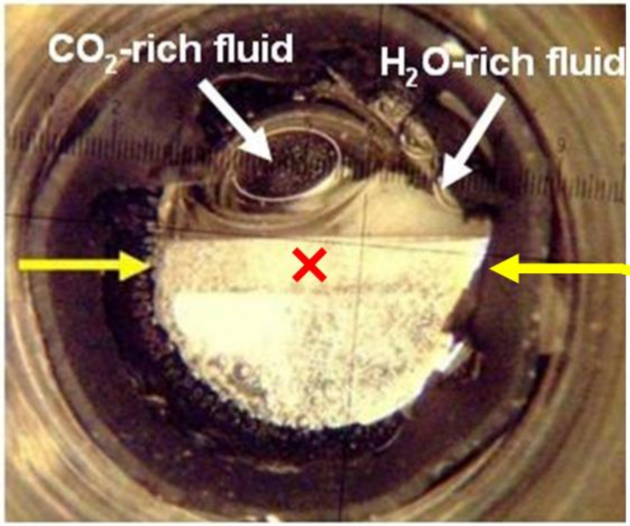
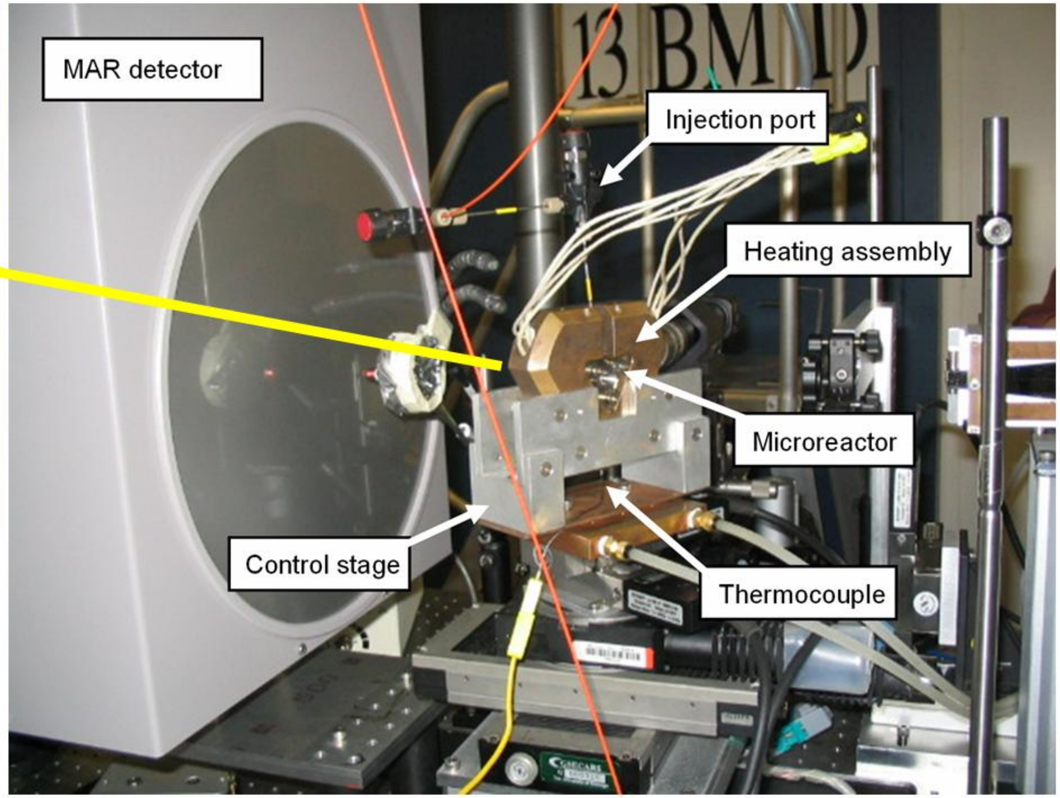
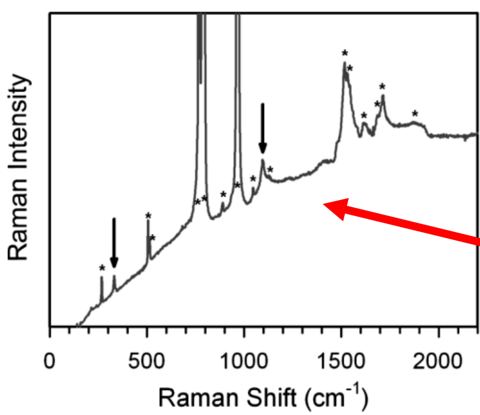


H_2O-CO_2 mixture
(T=180ºC, P_{CO2}=150 atm)





Formation of crystalline $MgCO_3$ confirmed using Raman (shifts at 331 cm^{-1} and 1094 cm^{-1})

Useful in detecting both crystalline and **"non-crystalline"** carbonates

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Application:

Optimization of Aqueous Mineral Carbonation Reactions

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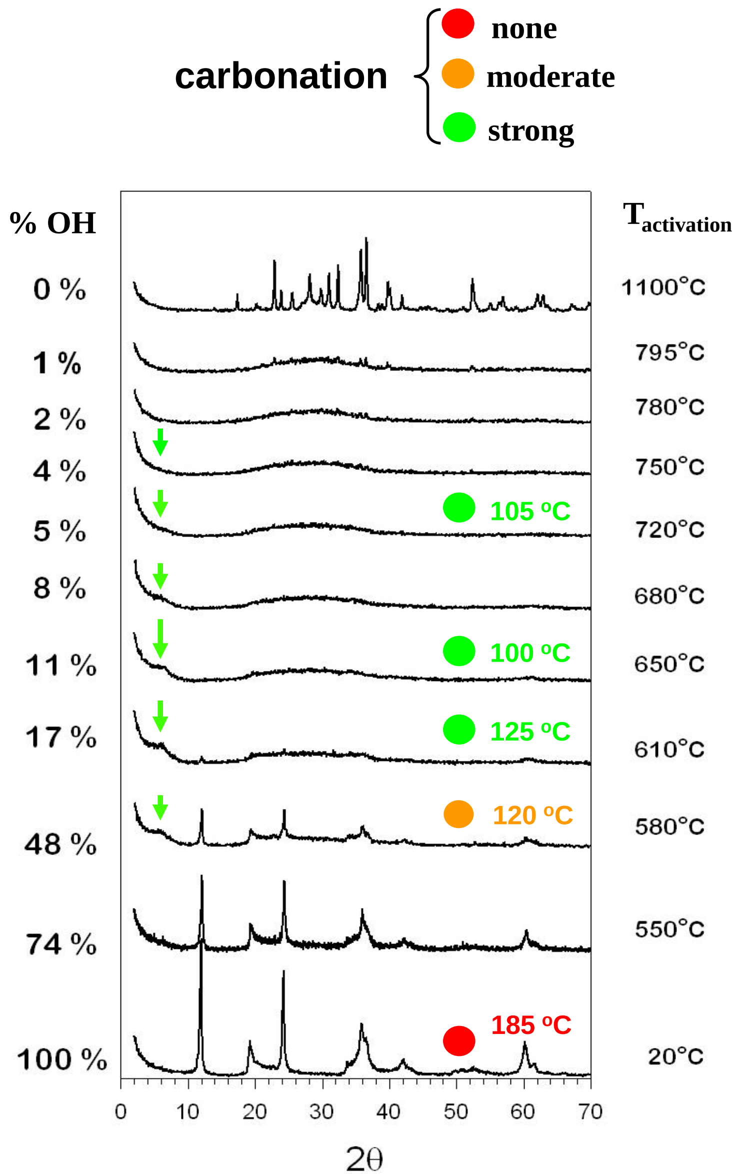
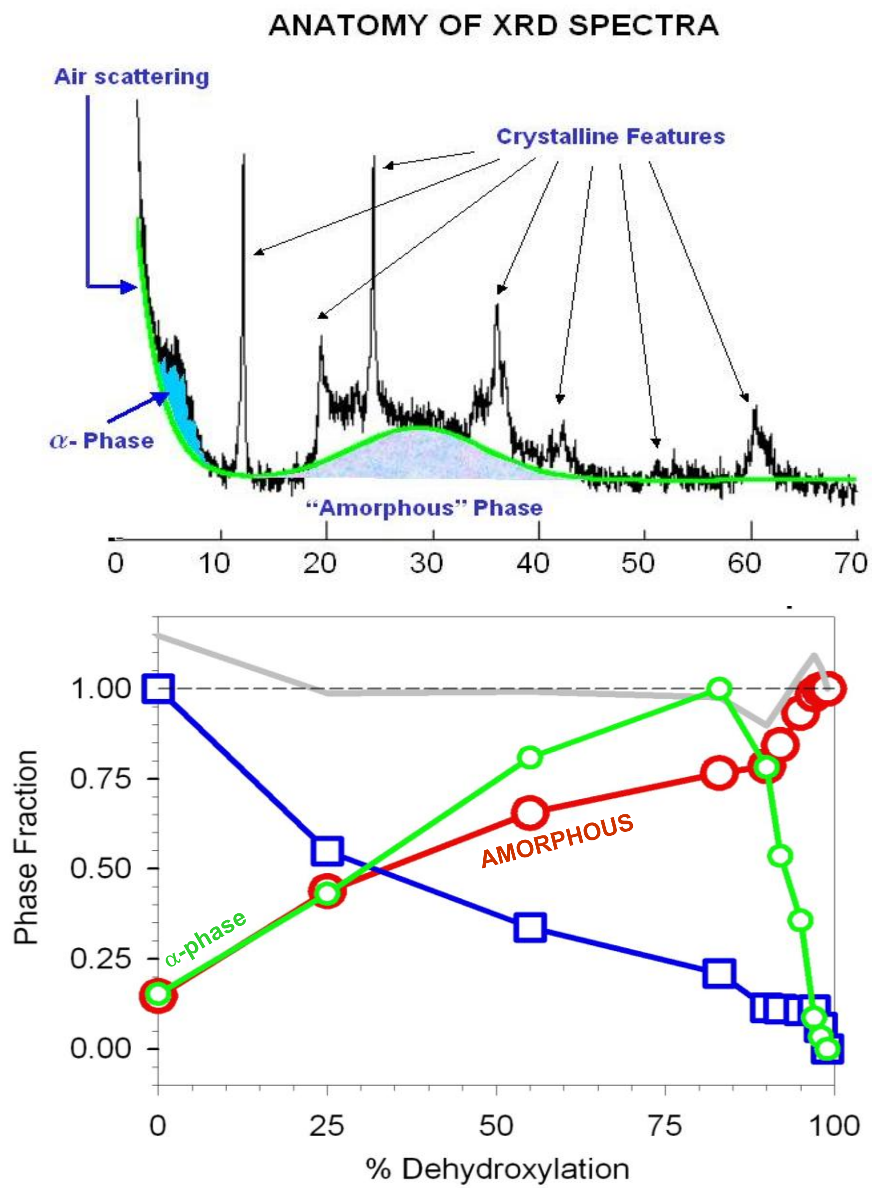
Reaction Studies of Lizardite Feedstock ($Mg_3Si_2O_5(OH)_4$)





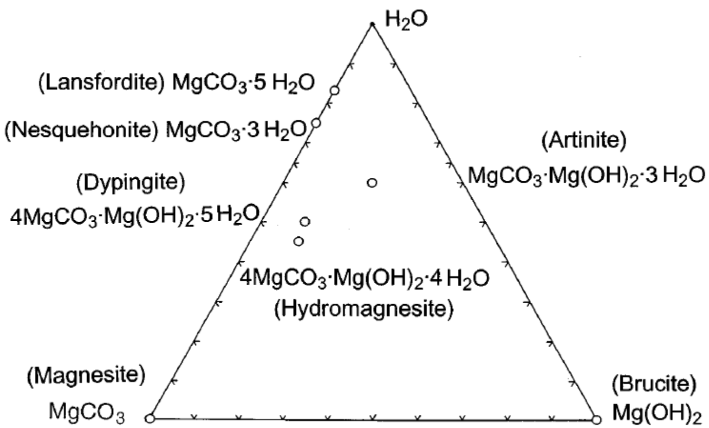
Application:

Mineral Carbonation Reactions under actual “below ground” Geological Conditions

Mineralization via Formation of Hydrous Carbonate Phases: Fundamental Studies

Background and Relevance: Programmatic DOE (Fossil) emphasis on “geologic” CO_2 sequestration (below ground) → how and when do hydrous carbonates form at **below ground conditions**. MgO is the only engineered barrier certified by EPA for the Waste Isolation Pilot Plant (WIPP) – formation of hydrous carbonates common.

Hydromagnesite	$Mg_5(CO_3)_4\ (OH)_2\ \ 4H_2O$
Giorgiosite	$Mg_5(CO_3)_4\ (OH)_2\ \ 4H_2O$
Artinite	$Mg_2(CO_3)\ \ (OH)_2\ \ 3H_2O$
Dypingite	$Mg_5(CO_3)_4\ (OH)_2\ \ 5H_2O$
Nesquehonite	$Mg\ (CO_3)\ \ \ 3H_2O$
Lansfordite	$Mg\ (CO_3)\ \ \ 5H_2O$



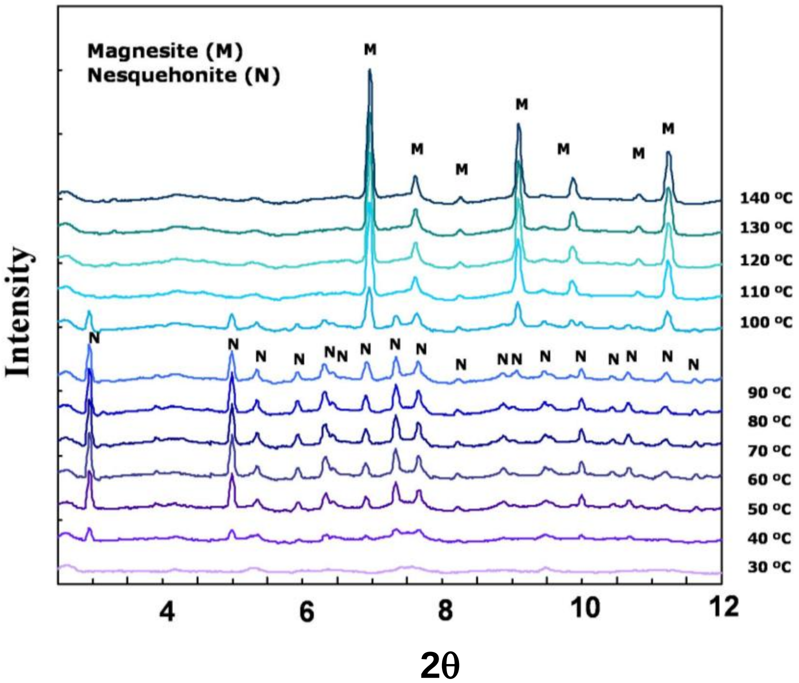
hydromagnesite

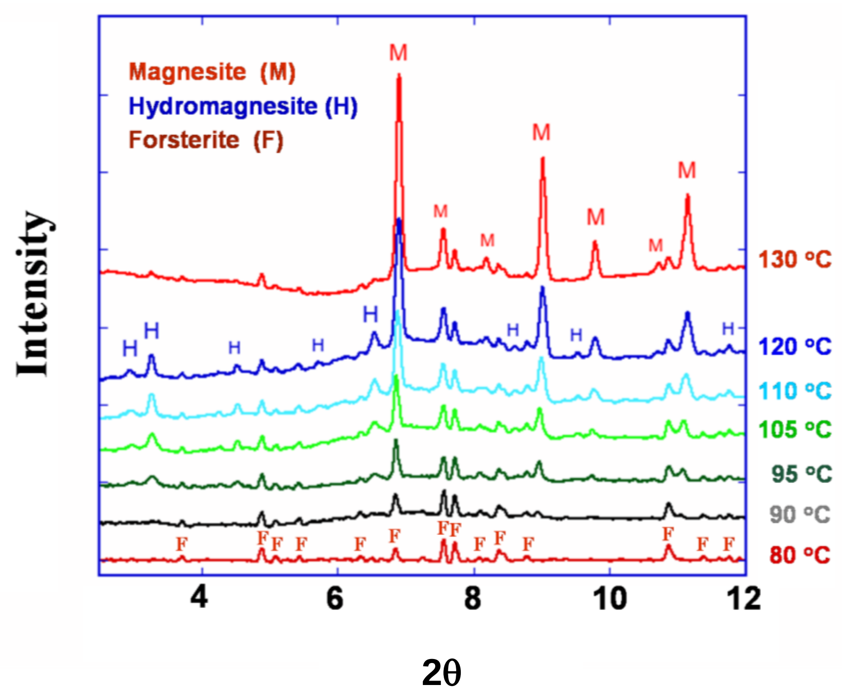
nesquehonite

- Mg-rich minerals as potential reservoir well-boar sealing agents (O’Connor *et al*, 2006)
- Formation of Mg-based hydrous carbonates in basaltic geologic sequestration formations.
- Structural data on hydrous phases is scant – **large uncertainties in the themodynamic data** ($\Delta G, \Delta S$)

URGENT NEED FOR FUNDAMENTAL STUDIES

Synchrotron Reaction studies using *in situ* Microreactor





Antigorite ground for 2 hours

- reacted @ P_{CO2} ~ 150 atm in buffered (0.64 M NaHCO3 + 1.00 M NaCl) H_2O-CO_2
- **Nesquehonite** onset observed at ~ 40°C
- Recession by 100°C, and onset of $MgCO_3$

Heat activated lizardite (5% OH)

- reacted @ P_{CO2} ~ 150 atm in buffered (0.64 M NaHCO3 + 1.00 M NaCl) H_2O-CO_2
- **Hydromagnesite** + magnesite onset observed at ~ 90°C
- Recession of hydromagnesite by 120°C, continued growth of $MgCO_3$

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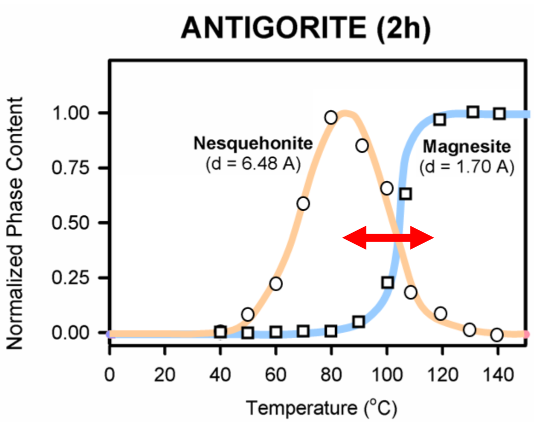
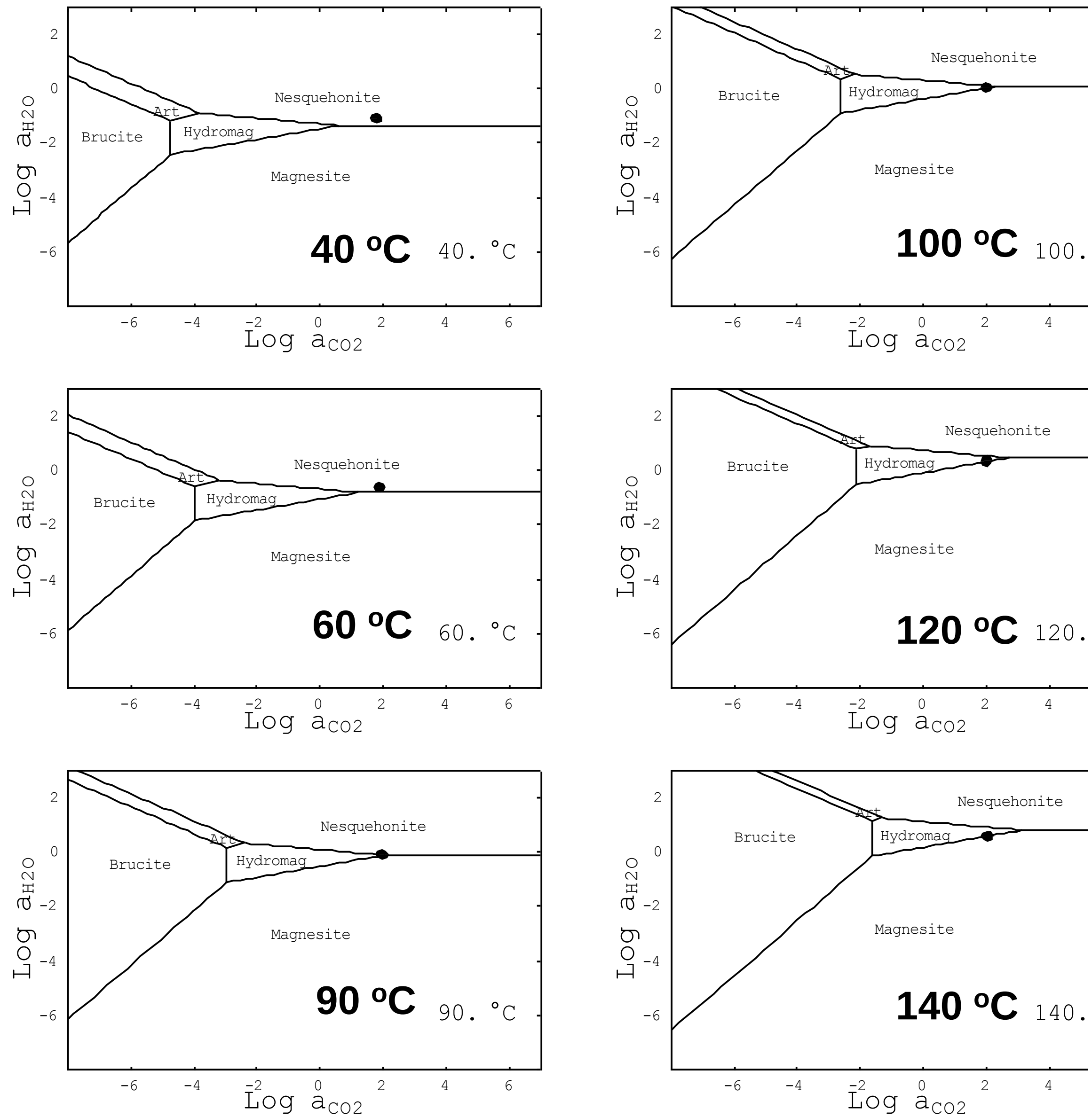
Phase stability field for the MgO-CO_2-H_2O system

- Activities obtained from Spycher et al EOS
- Dot represents activities corresponding to *in situ* experiment



- Kinetic origin of differences in observed transitons:

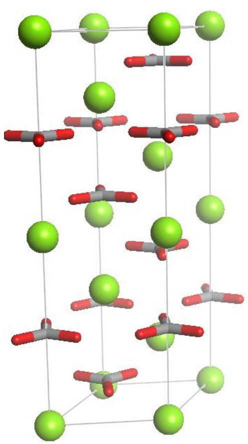
hydromag → magnesite
nesquehonite → magnesite



Supercomputer Simulations: Structure/kinetics connection?

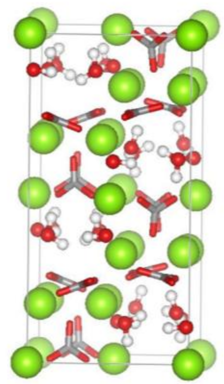
- use GGA-based DFT (hydrogen bonding + improved ΔE)
- Excellent agreement with experimental structure from xray (significant effect on lattice constants due to vibrational entropy contribution from confined water

magnesite

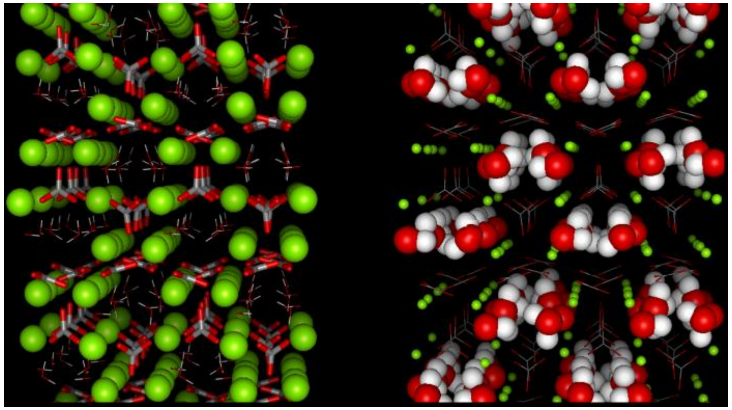


- hydromagnesite contains distribution of CO_3 orientations
- nesquehonite contains coplanar CO_3 units
- Molecular dynamics simulations suggest **simple kinetic pathway between nesquehonite and magnesite**

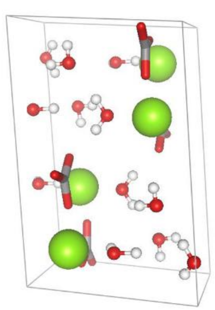
hydromagnesite



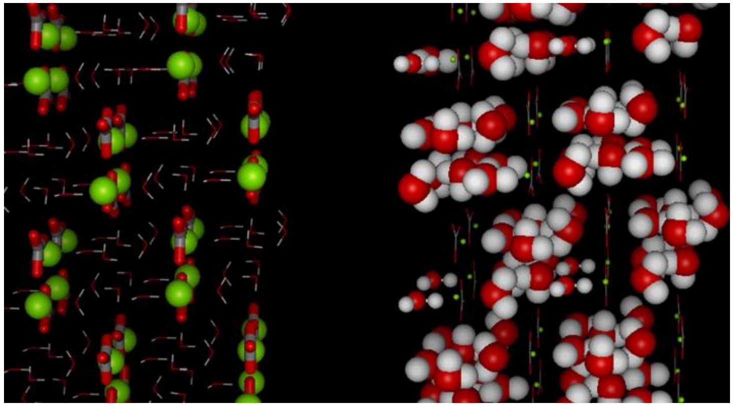
$Mg_5(CO_3)_4(OH)_2 \cdot 4\,H_2O$



nesquehonite



$MgCO_3 \cdot 3\,H_2O$



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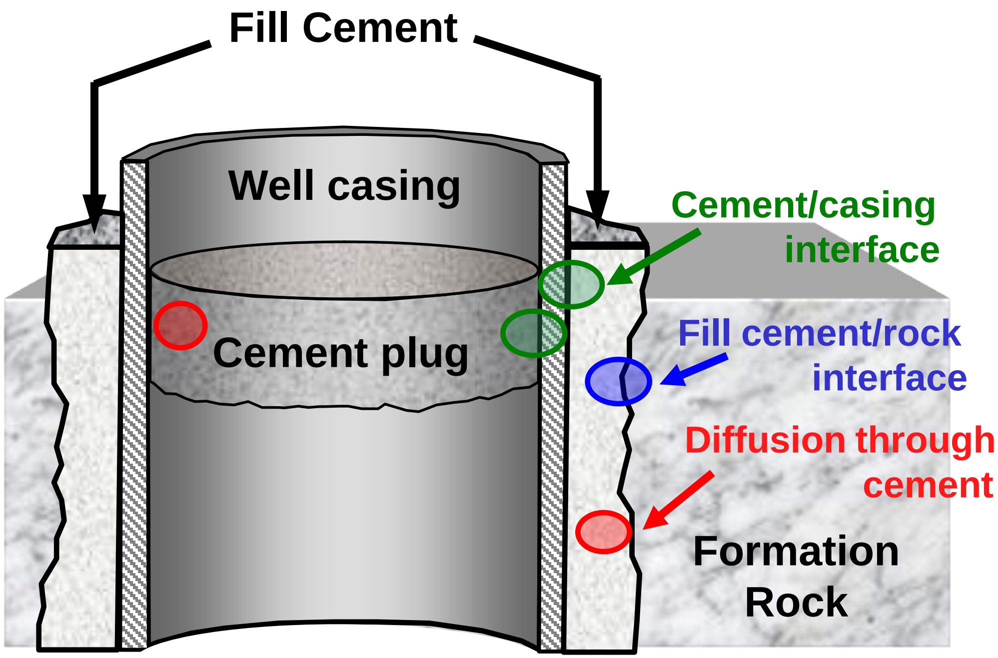
Application:

Well-bore Seal Enhancement in Geological Sequestration

Enhancement of Natural Seals:

- Reliable well-bore seals essential for long-term stability of geological storage
- Co-injection of reactive solids with CO_2 in reservoir
- *DOE NETL-Albany Research Center:* enhance seal via well-bore cement additives such as ***wollastonite***, ***serpentine*** and **olivine**



Based on an image by Dan Magee, Alberta Geological Survey

Fundamental knowledge of the physical and chemical behavior of CO_2 in the host geologic environment is highly desirable

Can we study fluid activities, transport, and reaction processes *at actual below-ground conditions* ?

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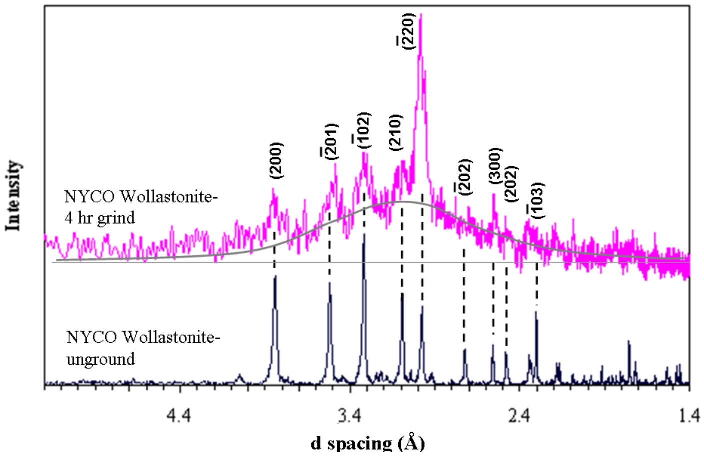
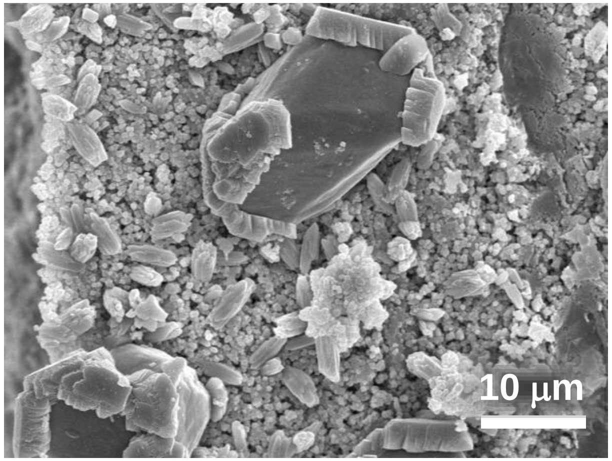
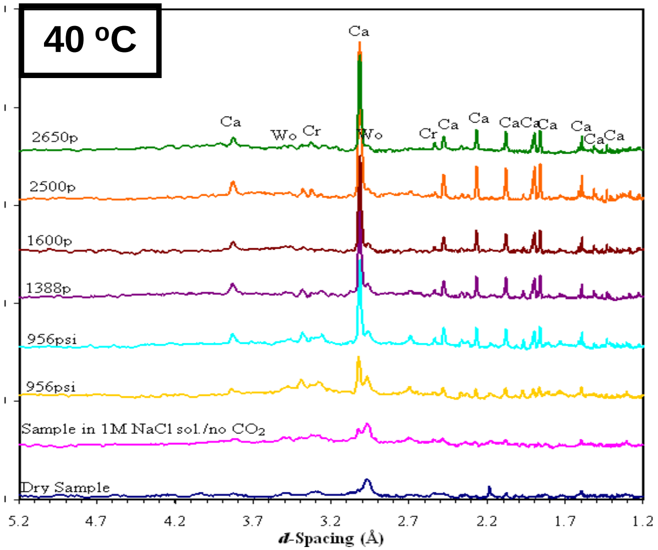
Carbonation of mechanically activated Wollastonite ($CaSiO_3$):

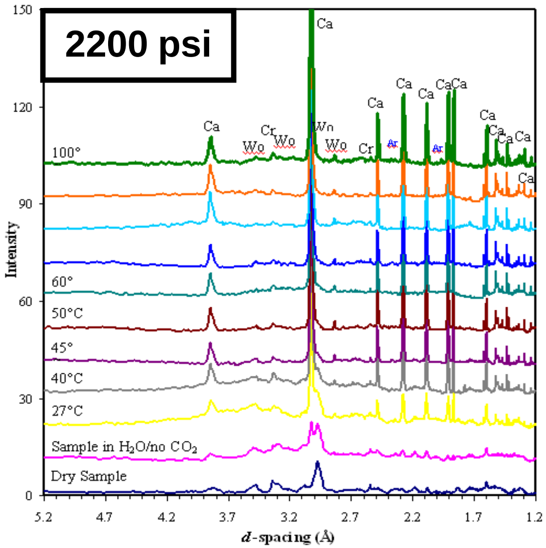
Effect of 4h grinding in Al ball mill





SEM image of $CaSiO_3$ reacted at 25 ° C, under 150 atm of CO_2 in 0.64M $NaHCO_3$ + 1M NaCl. Different particle sizes and morphologies of the product calcium carbonates (calcite, aragonite, and vaterite).





- Wollastonite **much more reactive** than olivine or serpentine under similar conditions
- 1M NaCl **suppresses** the formation of both aragonite and vaterite and favors the formation of calcite

Varying Pressure ("depth")

Varying Temperature

Application:

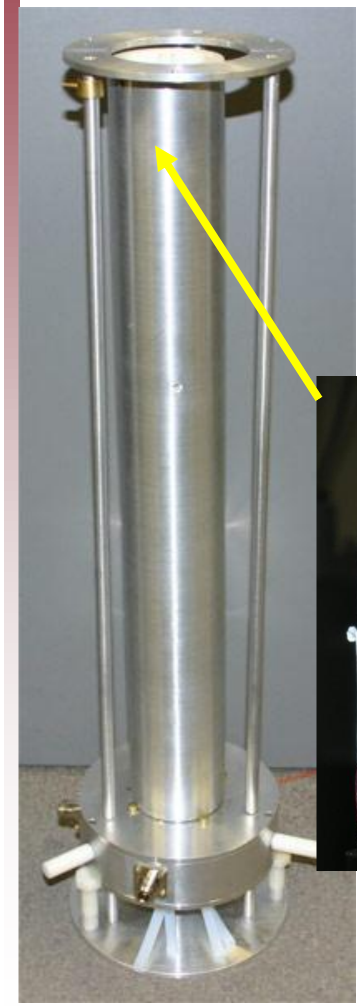
Temperature and Pressure dependence of CO_2, CO_3, HCO_3 diffusitives in CO_2-rich and H_2O rich solutions

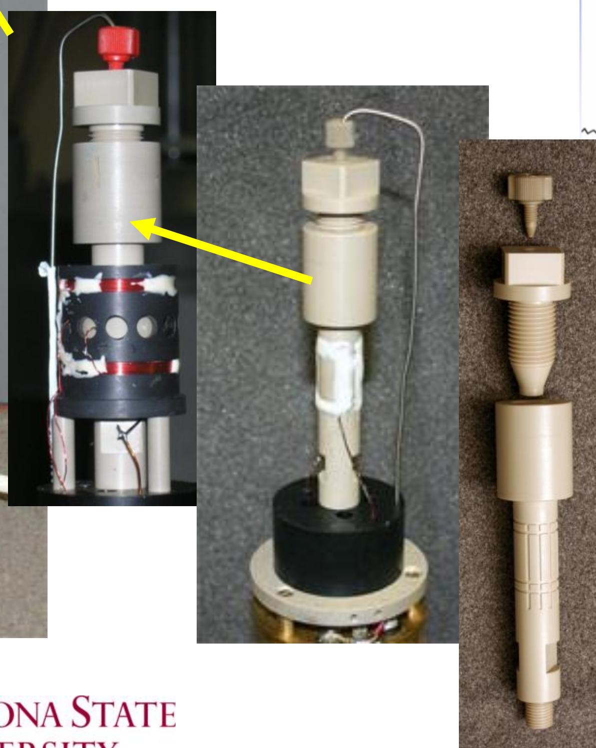
RECENT ADVANCES in CARBON SEQUESTRATION at ASU:

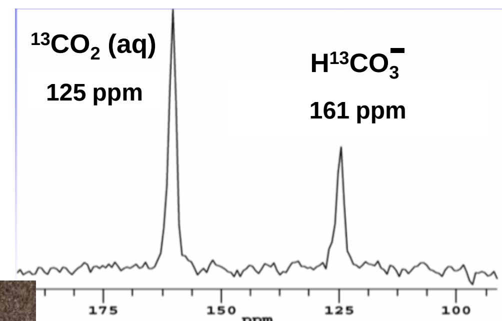
DEVELOPMENT OF AN NMR MICRO-REACTOR for IN-SITU REACTION STUDIES

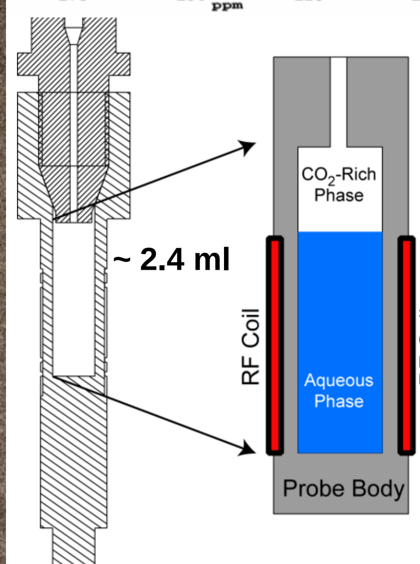
Rapid *In Situ* Chemical Observations

- Study H_2O-CO_2 system at high P & T
- Relative speciation of $CO_{2(aq)}$, HCO_3, etc
- Quantitative
- Interface diffusion
- Self-diffusion









- Designed and developed at ASU
- Wide-bore super-conducting magnet
- 300MHz Varian Infinity Solids NMR
- Chemically inert & non-magnetic Vespel, PEEK
- Pressure, activity & temperature control to 175 °C and 150+ atm
- "double tuning" allows simultaneous measurement of ^1H and ^{13}C signals

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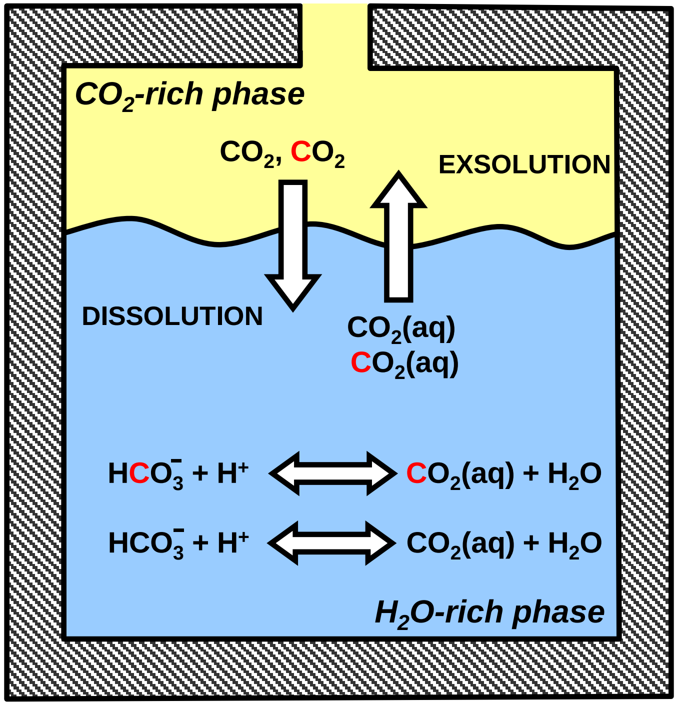
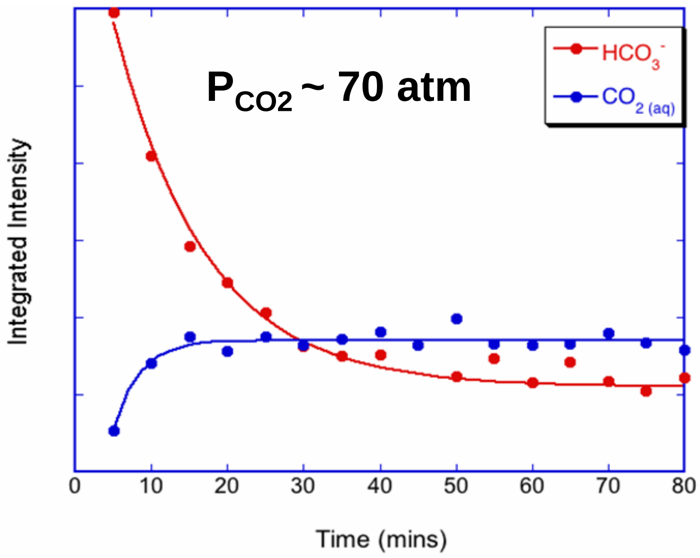
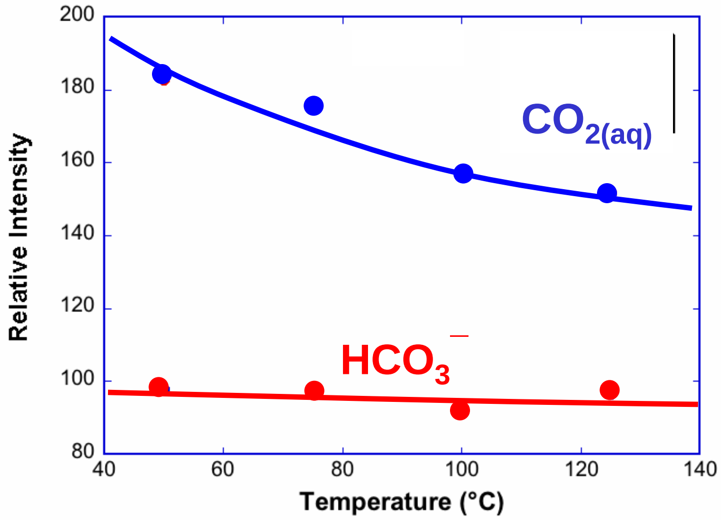




Equilibration dynamics of HCO_3^- and CO_2(aq) at room T and 70 atm (0.64M $NaHCO_3$ + 1M NaCl)



Carbon speciation vs Temperature (0.64M $NaHCO_3$ + 1M NaCl)

- CO_2 Dissolution
- $H^{13}CO_3/CO_2$ bulk exchange
- $^{13}CO_2/CO_2$ interface exchange

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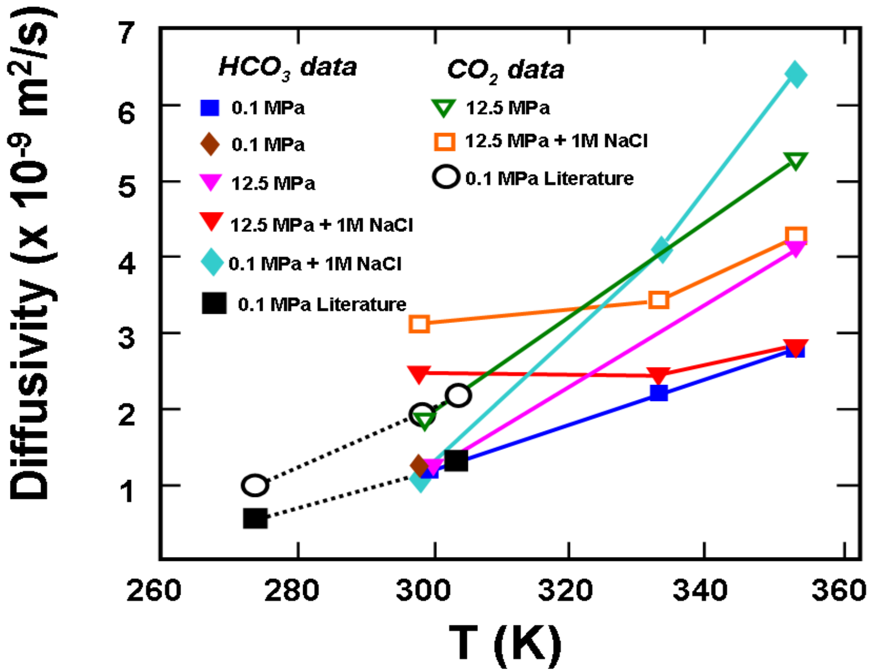
Pressure and Temperature dependence of CO_2 and HCO_3 diffusivities



- Use $NaHCO_3$ or $CO_{2(aq)}$ containing 99% ^{13}C
- Pressurize to 125 atm CO_2
- Equilibration (CO_2 dissolution, exchange between dissolved CO_2 and bicarbonate, exchange of $^{13}CO_2(aq)$ with CO_2 rich fluid)
- Observed $CO_{2(aq)}$ concentration in good agreement with known equilibrium values
- Analyze intensity vs. gradient pulse length data to obtain diffusivities at desired P and T

CO_2-rich solutions:	▪ diffusivities generally decrease with increasing pressure at any T
H_2O-rich solutions:	▪ HCO_3 diffusivity **increases** with P_{CO2} at T > 80 ºC
H_2O-rich + NaCl solutions:	▪ HCO_3 diffusivity **increases** with T at low P_{CO2}
	▪ HCO_3 diffusivity **decreases** with T at high P_{CO2}

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CONCLUSIONS

- Microreactor cell and high pressure NMR probe enable fundamental *in situ* studies of CO_2 interactions with below ground host geological environment, and above ground CO_2 mineralization reaction optimization.

Current *in situ* studies → phase formation and stability of hydrous/anhydrous magnesium carbonate phases as a function of temperature, $P(CO_2)$ and aqueous chemistry.

→ NMR probe has provided first direct determination of $CO_2/HCO_3/CO_3$ transport/diffusion at actual sequestration (above and below ground) conditions

FUTURE DIRECTIONS

- *In situ* observations of the permeability and porosity changes of reservoir core materials under actual CO_2 injection/sequestration conditions

- Long term (3-9 month) "in situ" microreactor studies to validate "ex situ" measurements of $scCO_2$/brine/mineral reactions.